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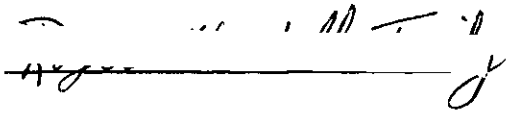

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EXTRACTION OF IRON WITH METHYLISOBUTYL KETONE AND ITS SUBSEQUENT PHOTOMETRIC EDTA TITRATION

A THESIS

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Roger Wendell Tinsley

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EXTRACTION OF IRON WITH METHYLISOBUTYL KETONE

AND ITS SUBSEQUENT PHOTOMETRIC EDTA TITRATION

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Date approved by Chairman: Feb. 23. 1971

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TABLE OF CONTENTS

TABLE OF CONTENTS (Concluded)

LIST OF TABLES

LIST OF FIGURES

SUMMARY

In the present study thiocyanate, salicylic acid, and sulfosalicylic acid are investigated for possible use as chromogenic agents in a photometric EDTA titration of iron after its extraction with methylisobutyl ketone. Sulfosalicylic acid is the reagent of choice. The photometric titration can be performed within the pH ranges 2.2 - 3.2 and 4.6 - 4.8. The lower range is preferable since there are fewer potential interfering metals.

The procedure employed in the study is as follows. The iron is extracted into methylisobutyl ketone from an aqueous solution made 6 N in hydrogen chloride. The iron is then reextracted into an aqueous phase containing sulfosalicylic acid and an acetic acid - sodium acetate buffer.

The subsequent procedure varies with the pH range desired for the titration. Since the higher pH range is established directly by the acetic acid - sodium acetate buffer system, the solution can be titrated photometrically with EDTA at 475 nm without additional steps. The lower pH range is established by adding strong acid to overcome the action of the acetate buffer and then a solution of monochloroacetic acid - sodium monochloroacetate buffer. The resulting solution can be titrated photometrically with EDTA at 520 nm. Accurate results have been obtained for less than 0.5 microgram iron per milliliter sample solution.

The effect of the presence of possible interfering metal ions

(in particular copper and zinc) has been investigated. Copper interfers at a 4:1 ratio of copper to iron. However, zinc shows no interference at a 16:1 ratio of zinc to iron.

CHAPTER I

INTRODUCTION

Iron is one of the fundamental technological metals and is widely distributed as a component of both naturally-occurring and artificially-produced materials. Thus it is understandable that a multitude of methods exists to analyze for iron. The majority of important methods developed up to 1962 is compiled and summarized in Treatise on Analytical Chemistry (1).

Despite the enormous number of existing methods, research is continually being conducted in this area. Although there are many well-working, highly sensitive methods, none of them is universally applicable because of lack of selectivity and freedom from interferences. The situation becomes even worse when judging the present-day need of determining small or even trace amounts in a variety of materials. Barring spectrography and some other purely physical methods, separations are unavoidable since in most cases even masking does not provide relief.

There are two possible approaches regarding the separations. One tries either to find a reagent that attacks and removes the majority of the interfering elements, or to develop a method that removes the iron with as little as possible co-removal of interfering elements. In the present situation the latter approach seems more practical.

Although there are many proposals dealing with this type approach one of the best seems to be that by Wickbold (2). This worker extracts

iron from an aqueous phase, high in chloride ion, into methylisobutyl ketone (MBK). The iron in the organic phase is then determined by an extractive EDTA titration using thiocyanate as the indicator.

Some of the details of this method are as follows. To the aqueous iron solution, contained in a separatory funnel, is added a small amount of nitric acid in order to be sure that all the iron is in the trivalent form. The solution is then made 6 N in hydrogen chloride by adding an equal volume of concentrated hydrochloric acid. A portion of MBK is added, the funnel shaken, and the lower, aqueous layer withdrawn. To the ketone phase remaining in the funnel are added portions of distilled water, acetic acid - sodium acetate buffer, and ammonium thiocyanate solution. When shaken the phases thoroughly mix and the thiocyanate complex of iron is formed. Upon standing, phase separation occurs with the red organic, upper layer containing the complex.

The extractive titration is performed by adding increments of the EDTA solution with shaking after each addition. As the titration proceeds the upper, ketone layer becomes less colored (decomposition of the iron-thiocyanate complex) and the lower, aqueous layer becomes progressively yellow (formation of the iron-EDTA complex). The point where the ketone phase has become completely colorless is taken as the end point.

While this method represents a significant advance with respect to existing possibilities, there is still room for improvement. For example, when the approach is applied to samples with decreasing iron content, increasingly high results are obtained. This can be seen from Table 1 which contains a portion of Wickbold's results.

Table 1. Results of EDTA Titration of Iron Using Various Titrant Concentrations. Theoretical Consumption of Titrant in Each Case is 25.00 ml. (After Wickbold)

Concentration of titrant, F	0.1	0.01	0.001	0.0001
Number of titrations	20	10	10	10
Arithmetic mean, ml	24.95	25.00	25.09	25.86
Relative standard deviation from the mean, %	± 0.09	± 0.08	± 0.08	± 1.5

This is a rather surprising happening because actually low results would be expected. The titration works toward the disappearance of the last trace of pink in the organic layer. With the inadequacy of the human eye one might expect that colorless is seen when actually there is still some color left. Thus, the titration would be stopped too early. High results could possibly be explained by iron impurities in the reagents. However, considering the reliability of the author, this possibility can well be excluded. Then one can best explain the high results by some unfortunate situation in the equilibria involved causing slightly more than the equivalent amount of EDTA to be required in removing all the iron from the organic phase.

In order to make the titration work also for the highly important area of trace analysis, some modifications had to be made. One of the many possibilities suggesting itself was to switch from an extractive to a single phase titration. In the present investigation this was tested by adding a mediator, that is, a reagent that causes the organic and aqueous phases to mix homogeneously. For example, ethanol or acetone act as mediators between MBK and water.

At the same time the visual titration should be abandoned and replaced by a photometric titration which is inherently more sensitive. Thus the accuracy should be further improved and in addition a considerable gain in precision (see the data of Wickbold in Table 1) should be realized.

The photometric titration in certain cases might also eliminate some problems caused by interfering elements. Interferences must always be kept in mind when developing an analytical method. It was hoped that

in this area the presently proposed method would make an additional improvement over the method of Wickbold which was nonideal in this respect. While the extraction as performed according to the original paper is quite selective, there are still some elements which, to varying degrees, are extracted with the iron.

Indium and gallium form very stable chlorocomplexes and are extracted 94 and 100 percent, respectively. With indium becoming an important element in electroplating and traces being undesirable as a pollutant from industrial wastes, the combination iron-indium is no longer of purely academic interest. Other metals are extracted too, although to a lesser degree, as can be seen from Wickbold's data which are reproduced in Table 2.

With these situations and goals in mind the mediator approach with photometric finish was investigated.

Table 2. Extraction of Metal Ions into Methylisobutyl Ketone[a] (After Wickbold)

Metal Ion Present	Water Phase	
	5-7 N HCl[b] % Extracted	6-7 N LiCl[c] % Extracted
Fe(III)	100	100
Ga	100	100
Cr(VI)	98	none
Mo	96	none
In	94	60
Sn(IV)	93	91
As(III)	88	33
V(V)	81	none
Sb(III)	69	47
U(VI)	22	5
Cd	13	none
Zn	6	1
Cu	4	1
As(V)	4	none
Co	3	none
Ni	1	none
Th	1	none
Mn(II)	0.7	none
Bi	0.5	none

[a]Only metals which form EDTA complexes are shown.

[b]Not extracted from HCl: Mg, Ca, Sr, Ba, Al, Ce(III), Ti, Zr, Pb, Cr(III), Ag.

[c]Not extracted from LiCl, in addition to those shown: Mg, Ca, Sr, Ba, Al, Ce(III), Ti, Zr, Pb, Cr(III), Ag, Th, As(V), Bi, V(V), Cr(VI), Mo, Mn, Co, Ni, Cd.

CHAPTER II

PHOTOMETRIC TITRATION IN THE PRESENCE OF A MEDIATOR

The mediator approach operates as follows: to the organic extract containing the chlorocomplexes of iron are added aqueous solutions of ammonium acetate and ammonium thiocyanate. The system is then shaken. After phase separation, ethanol is added and the red organic layer unites with the colorless aqueous layer. While a decrease in color intensity is expected due to dilution it is surprising to actually notice a complete disappearance of the red. The red reappears upon addition of nitric acid. Since neither acetic acid nor hydrochloric acid has such an effect, a pH change can be excluded as the reason for the phenomenon. The conclusion may be drawn that a reduction of the iron (III) by some impurities in the ethanol has taken place and that the nitric acid causes a reoxidation.

However, the intensity of the reestablished color is much lower than the original one even considering the dilution effect. The reason for this behavior of the system may be explained by the findings of West and co-worker (3). They found that various organic solvents have enhancing effects of different degrees on the color of the cobalt-thiocyanate complex. Such effects should also be expected for the iron-thiocyanate complex, especially in light of recent investigations by Barnes (4).

Thus, MBK has a great enhancing effect on the color of the iron complex and a deep red color results. Upon incorporation of ethanol and

water, which respectively cause a small and no enhancement, the intensity of the red has to decrease.

Some titrations in the mediated, color-weakened system were performed. While the two straight lines of the photometric titration curve were well developed and allowed a sharp intersect for end point location, the end points were not reproducible. No further time was wasted in investigating this phenomenon since it was already necessary to abandon the mediator approach because the color weakening and the large volume due to mediation resulted in too great a loss in sensitivity.

It was decided to operate next with a reextraction into an aqueous medium. By doing so, a gain in sensitivity could result when back extracting into a very small volume. Furthermore, the trouble with the irreproducible end point in the mixed system would be obviated. In addition, there exists the possibility of performing the back extraction under conditions such that further separation of the iron from some accompanying elements could be achieved.

For the reextraction, at first simply water was employed. Since there is no excess chloride present in the aqueous phase, the iron (III) chlorocomplexes in the organic phase break up readily. With the iron no longer complexed it is easily reextracted into the water. However, it was soon found that this approach as, for example, proposed by Gagliardi and Woss (5), who used the similar iron-methylethyl ketone system, did not work as well as when the aqueous layer contained a buffer system. It is especially advantageous to add to the aqueous phase a complexing agent that serves as a chromogenic agent by forming with the iron a self-

indicating system for the photometric EDTA titration. Salicylic acid was first tried as such an agent. The extraction went well with a buffer-salicylic acid system.

CHAPTER III

PHOTOMETRIC TITRATION IN THE PRESENCE OF SALICYLIC ACID

Although salicylic acid has been used previously as an indicator during the titration of iron (6,7) as have salicylic acid derivatives, such as 3,5-dinitrosalicylic acid (8,9), none of these investigations determined iron below the milligram level. Therefore, the following study was conducted.

1. Photometric Study of the Iron-Salicylic Acid System

A photometric study of the iron-salicylic acid system was undertaken utilizing the following method. To small amounts of iron in aqueous solution is added an excess of salicylic acid. The resulting solution is made strongly acidic and the absorbance curve recorded. The solution is then made less acidic by adding a minute amount of strong (so that dilution would be negligible) sodium hydroxide solution. The absorbance curve is then recorded again. This procedure is continued until curves are obtained for a wide range of pH values of the solution. A study of these curves shows that the pH range of about 1-6 is of greatest interest. Below pH one, the complex dissociates and above pH six decomposes with the formation of hydrous ferric oxide.

As can be seen from Figure 1, when the solution is adjusted to about pH 1.3, the curve has a peak at 520 nm. This peak increases as the pH increases. However, at about pH 3.2 the peak begins to shift toward

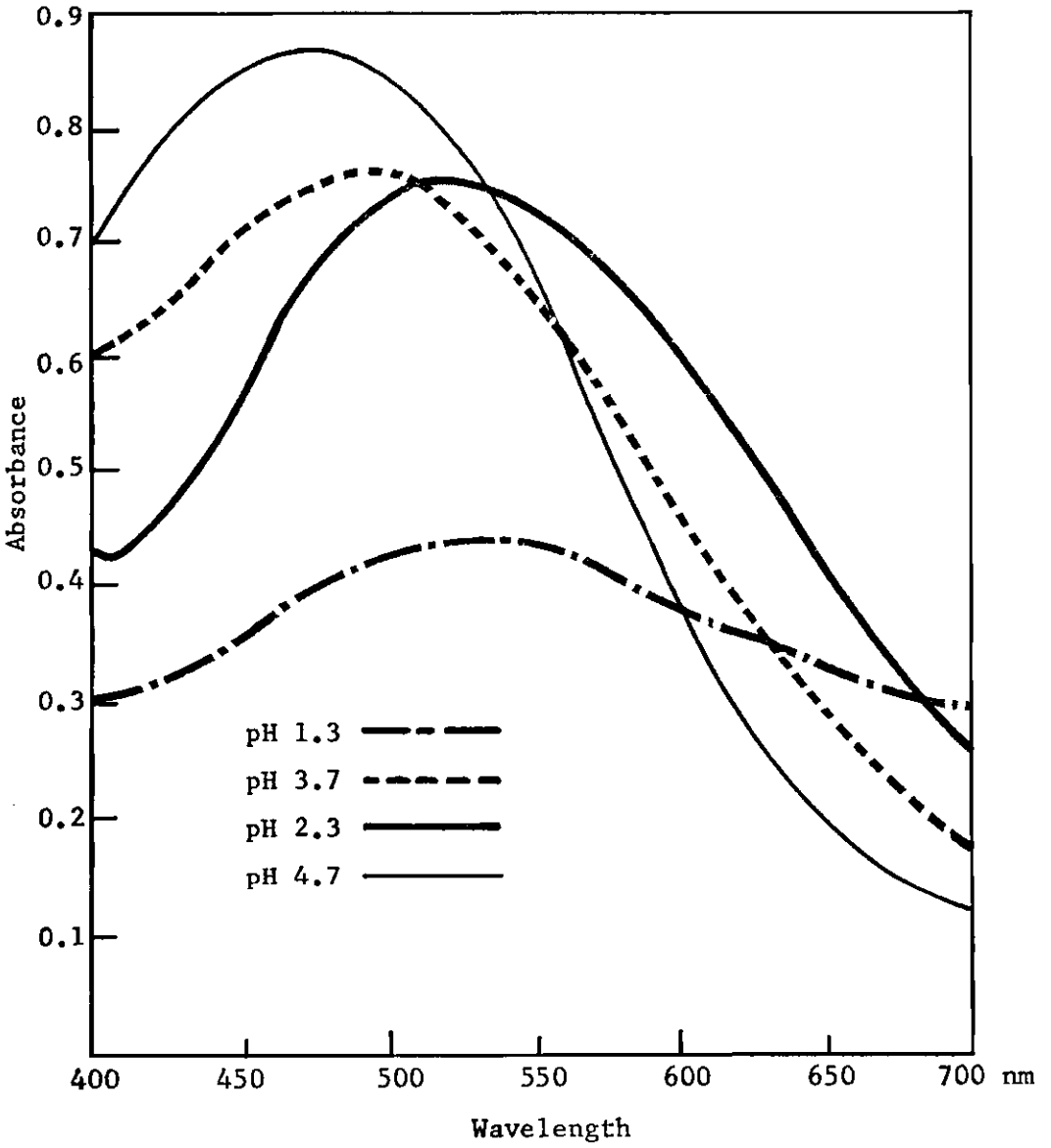

Figure 1. Spectral Curves at Various pH Values for the Iron-Salicylic Acid System

lower wavelengths. At about pH 4.4 the peak becomes established at 475 nm. Below pH one and above pH six there are no peaks observed. The changes can be attributed to the deprotonation of one or more waters of hydration in the iron-salicylic acid complex.

The data, partially represented in Figure 1, have been used to construct absorbance versus pH plots (Figure 2) for the two peak wavelengths. From these curves it can be seen that a titration may be performed in either the pH range 2.2 - 3.2 or 4.6 - 4.8. The colors of the solutions corresponding to the two pH ranges are violet and brown.

2. Selection of pH Range

Since there are two possible pH ranges in which the titration can be performed, it is necessary to determine which of these is more advantageous. The relative advantages of these ranges depend upon the type of material to be analyzed, preparation of the sample solution, and level of accuracy and precision required. Thus, it is not possible to claim *a priori* that either range is superior. However, in the following discussion the advantages and disadvantages of the two ranges will be dealt with and from the knowledge of the facts presented an appropriate selection of the range should be possible for any practical case.

2.1. Sensitivity

For either range there is a plateau that allows secure operation during the titration, although this plateau is extremely narrow in the higher range. Both plateaus correspond to absorbance maxima and thus guarantee the highest possible sensitivity. From Figure 2 it can be seen that the photometric titration will be slightly more sensitive when

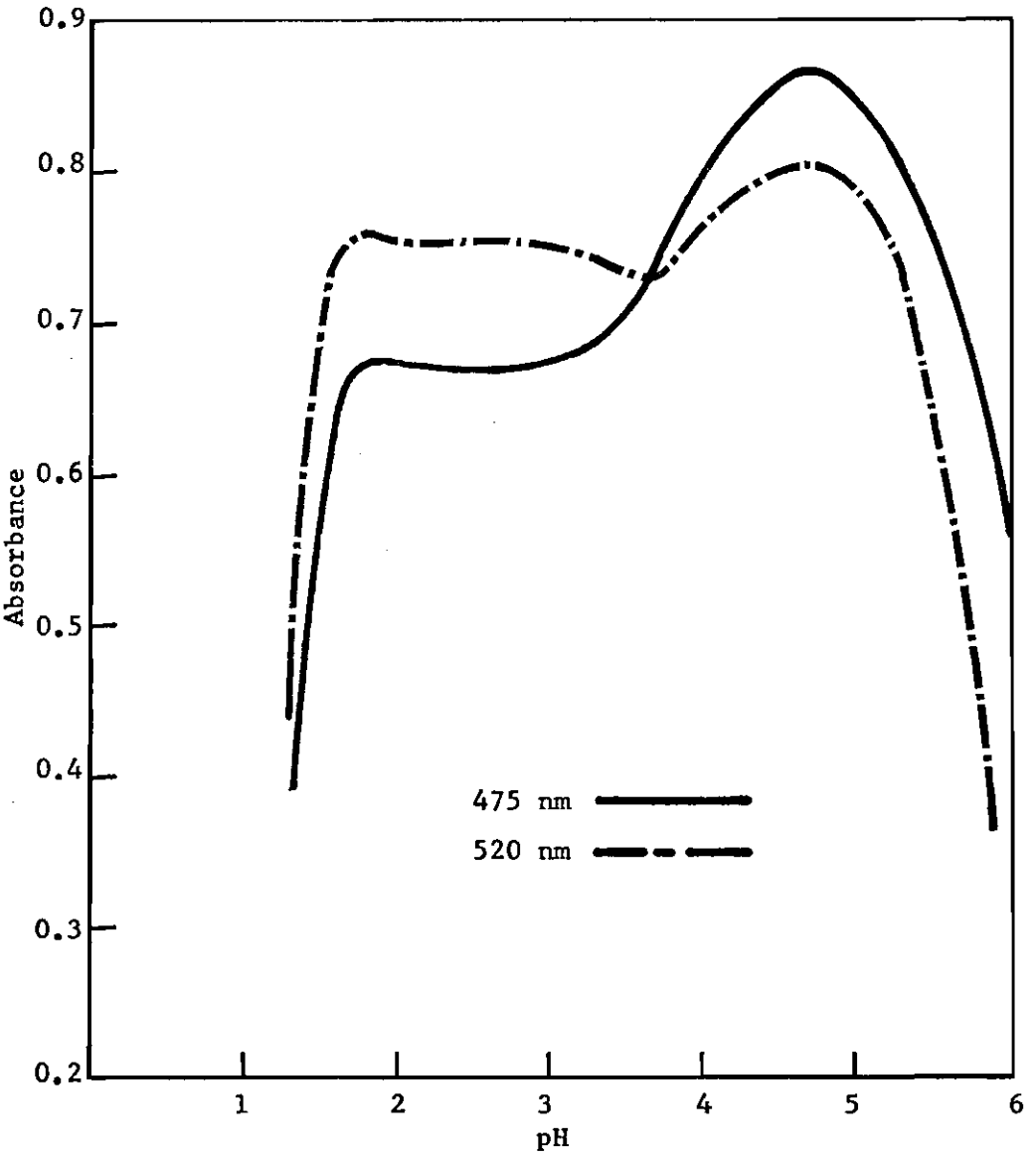

Figure 2. Absorbance versus pH Curves for the Iron-Salicylic Acid System

utilizing the higher pH range due to the higher absorbtivity. However, this slight gain in sensitivity would rarely be the determining factor in any given analysis.

2.2. Interference

From inspection of Table 2 and Figure 3 (which contains curves for metal ions which are extracted), it can be seen that the only metal ions which might interfere in the determination of iron in the sample are indium, gallium, copper, and zinc. All other metal ions either are separated from the iron since they are left in the aqueous, chloride-containing phase or, if they accompany the iron, have conditional stability constants so low that their interference would be negligible. It can also be seen that the difference in the conditional stability constants, log K' ($\log K'_{FeY} - \log K'_{MY}$), is such that the lower pH range is preferable since here both copper and zinc would interfere less.

It is important to note that the data in Figure 3 and this discussion do not include the effect of the salicylate ion. Although it is not expected that the salicylate ion would interfere to a great extent, one must be cautious when interpreting these data.

3. Adjustment of pH

Theoretically it would be possible to add an appropriate buffer to the aqueous layer for the reextraction so that either of the pH ranges is established. In practice, however, this is possible only for the higher range. Here buffers of adequate capacity are available to overcome the quite high acidity of the organic layer. (The latter layer is established by extracting a 6 N aqueous solution of acid!) For the lower pH

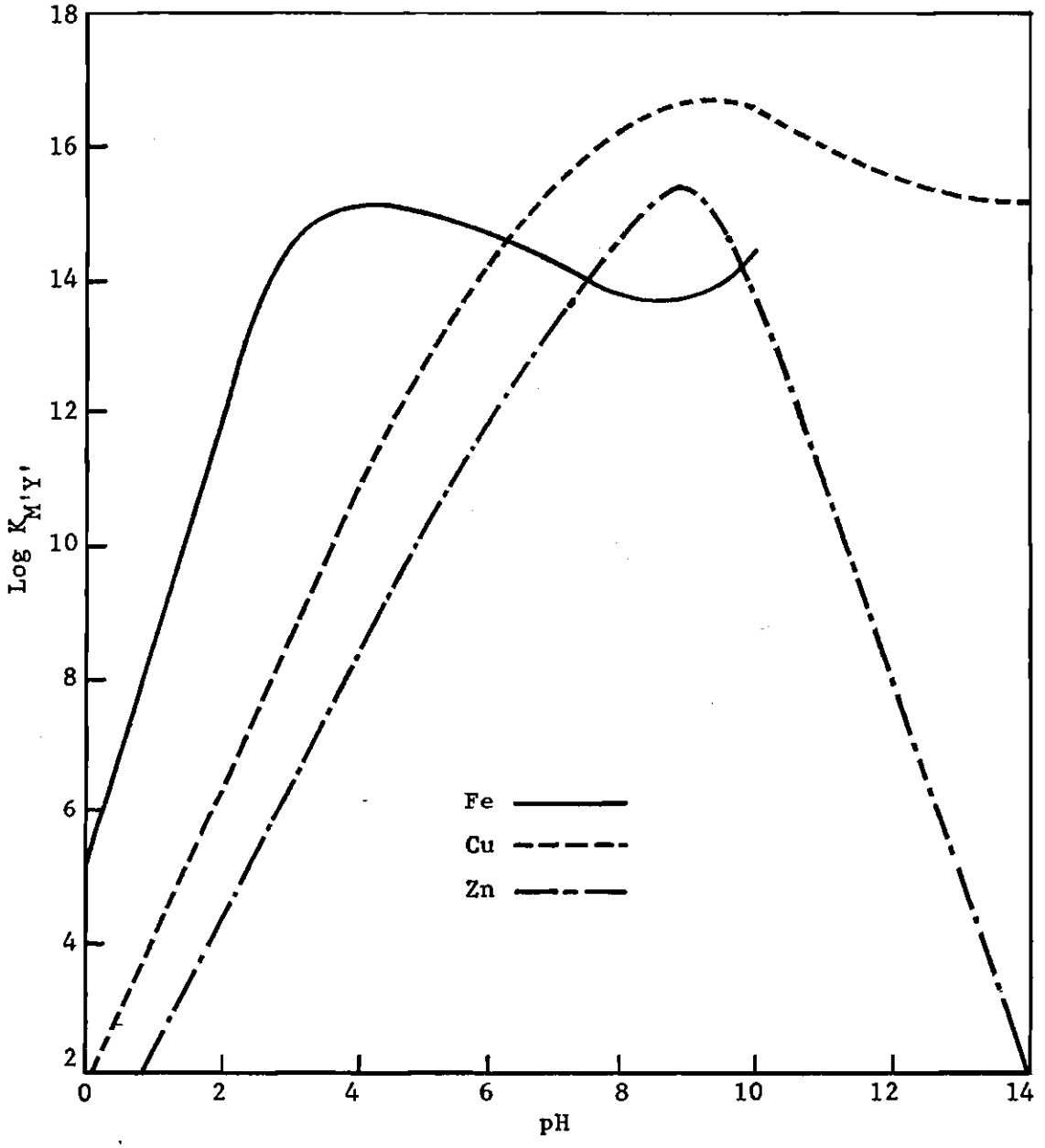

Figure 3. Conditional Stability Constants, $K_{M'Y'(MY)'}$, of Various Metal EDTA Complexes as Functions of pH. (After Ringbom)

range no buffer of adequate capacity exists. In addition, the lower the pH the lower the extraction efficiency. Thus, it was decided, in general, to use a high capacity, high pH buffer for the reextraction and then to adjust the pH for the titration.

3.1. Higher pH Range

The higher pH range can be established directly during the reextraction procedure by using an acetic acid - sodium acetate buffer. The fact that the pH range for the titration is only 0.2 pH units is not prohibitive since this buffer has no difficulty bringing the pH to a value within this range and maintaining it during the titration.

3.2. Lower pH Range

To establish the lower pH range after high pH extraction, it is necessary to add strong acid in order to overcome the action of the acetate buffer, since no buffer of adequate capacity exists. However, some method of indication is necessary to show when the correct pH value is obtained.

Both color and fluorescent indicators were investigated, but none of those available in this laboratory was suitable.

It was then realized that the iron (III) salicylic acid complex itself can be used as the indicator. The complex changes color with pH and goes from a deep to a weak violet at about pH two. Alternatively, the absorbance changes (see Figure 2) with pH can be used for indication through observation of the galvanometer deflection. The latter approach was chosen. When the galvanometer reading drops sharply upon addition of a small amount of strong acid, a pH of about two has been reached and a monochloroacetic acid - sodium monochloroacetate buffer is added.

This buffer was chosen since it has its maximum buffering capacity at pH 2.9. Thus a small amount of a concentrated buffer solution is sufficient to bring the pH from about two to within the range necessary for the titration.

4. Photometric Titration Results

Quite satisfactory results can be obtained, but there is one big drawback. The solubility of salicylic acid in water is a function of pH. In the lower pH range, salicylic acid is only slightly soluble. Unless the conditions are maintained quite carefully, too often analyses are spoiled because, before or during the titration, the solution develops a haze due to the formation of minute crystals of salicylic acid. Thus, the other advantages of the lower pH range are grossly outweighed and for practical purposes only the higher range is useful. In order to overcome this adverse situation and still have the two-range advantage, it was decided to replace the salicylic acid by its derivative, sulfosalicylic acid, which is extremely soluble at any pH.

The absorbance curves of the iron-sulfosalicylic acid complex as a function of pH are virtually identical to the set of curves for the iron-salicylic complex (Figure 1). There is also a great similarity between the absorbance versus pH curve for the iron-sulfosalicylic acid complex (Figure 4) and the iron-salicylic acid complex (Figure 2). Thus, the experience gained with salicylic acid could be used quite well for expanding the study to using the sulfo compound as chromogenic agent.

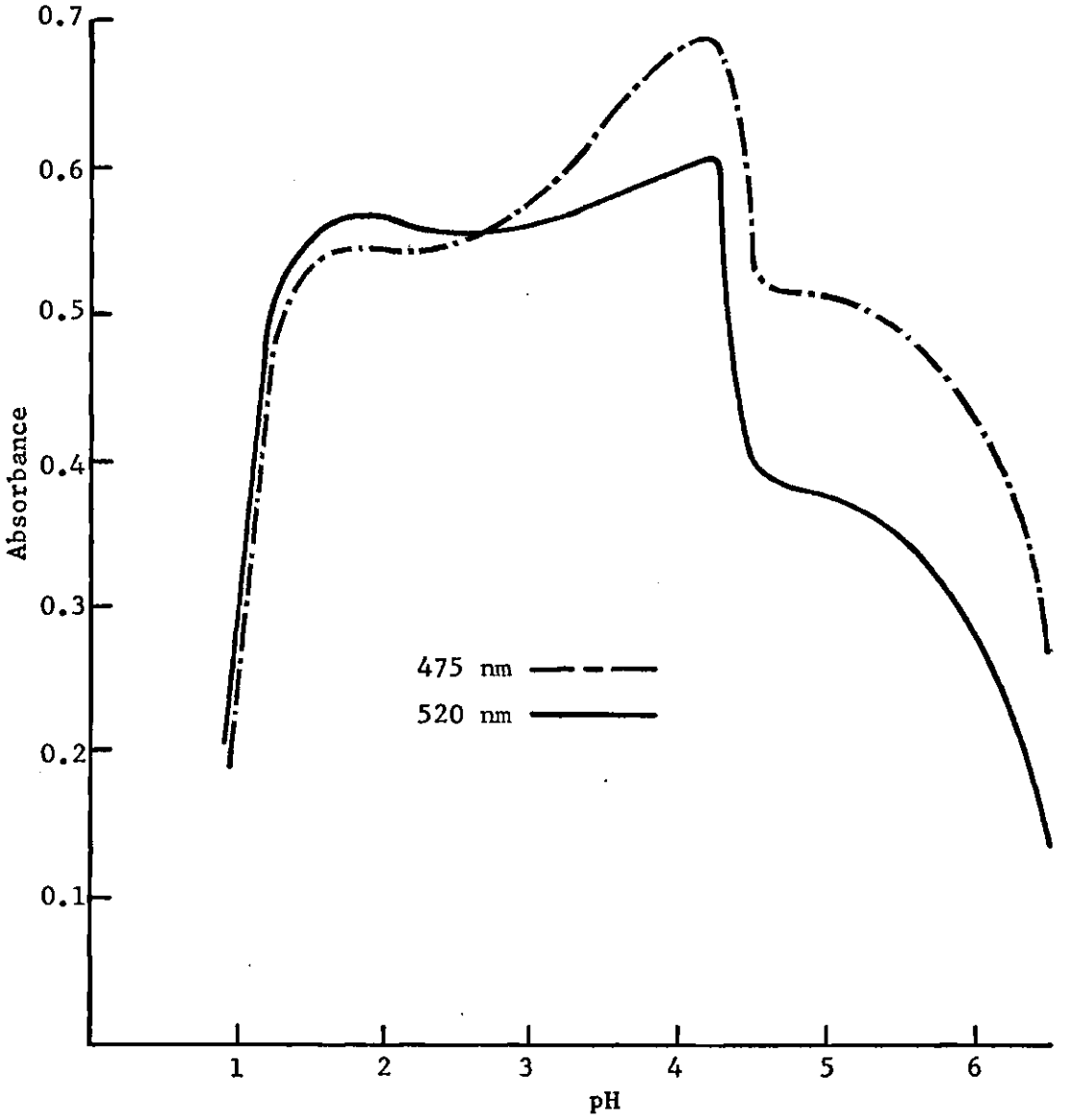

Figure 4. Absorbance versus pH Curves for the Iron-Sulfosalicylic Acid System

CHAPTER IV

PHOTOMETRIC TITRATION IN THE PRESENCE OF SULFOSALICYLIC ACID

1. Procedure

The procedure employed in the study was as follows.

1.1. Procedure A (Lower pH Range)

1. Deliver 10 ml of the aqueous iron solution from a buret into a separatory funnel, add a few drops of concentrated nitric acid, and mix well.

2. Add 10 ml of concentrated hydrochloric acid, 5 ml of MBK, and shake about 30 seconds.

3. Allow phase separation, drain the lower, aqueous layer into a second separatory funnel, retaining the MBK layer in the first funnel.

4. Add 5 ml of MBK to the second funnel and shake about 30 seconds.

5. Allow phase separation, discard the lower, aqueous layer, and drain the MBK into the first funnel.

6. Wash the second funnel using a 2 ml portion of the acetic acid - sodium acetate buffer containing 3 drops of 0.1 F sulfosalicylic acid, drain into the first funnel, and shake about 30 seconds.

7. Allow phase separation (about one minute), drain the lower, aqueous layer into the titration vessel, and rinse the funnel tip with about 0.5 ml of distilled water.

8. Add 2 ml of acetate buffer, 1 drop of 0.1 F sulfosalicylic acid, and shake about 30 seconds.

9. Allow phase separation (about 4-5 minutes), drain the lower, aqueous layer into the titration vessel, and rinse the funnel tip with about 0.5 ml of distilled water.

10. Position the titration vessel in the photometric titrator and insert a narrow bandwidth filter which transmits light at 520 nm.

11. Add nitric acid dropwise until there is a large galvanometer deflection after the initial small movement and then add a few drops of concentrated monochloroacetic acid - sodium monochloroacetate buffer.

12. Add increments of the standard EDTA solution with stirring after each addition until successive additions show only a small change in galvanometer reading.

13. Plot log (scale divisions) versus microliters of standard EDTA added.

A representative titration curve obtained by employing Procedure A is shown in Figure 5.

1.2. Procedure B (Higher pH Range)

Follow Procedure A with the following exceptions:

1. Use a 475 nm filter.

2. Omit addition of nitric acid and monochloroacetic acid - sodium monochloroacetate buffer.

2. Reliability

In order to test the reliability of the method, various amounts of iron were titrated without extraction and the milliliters of iron solution added were plotted versus the microliters of standard EDTA solution consumed. If no problems are encountered, the curve obtained should be a

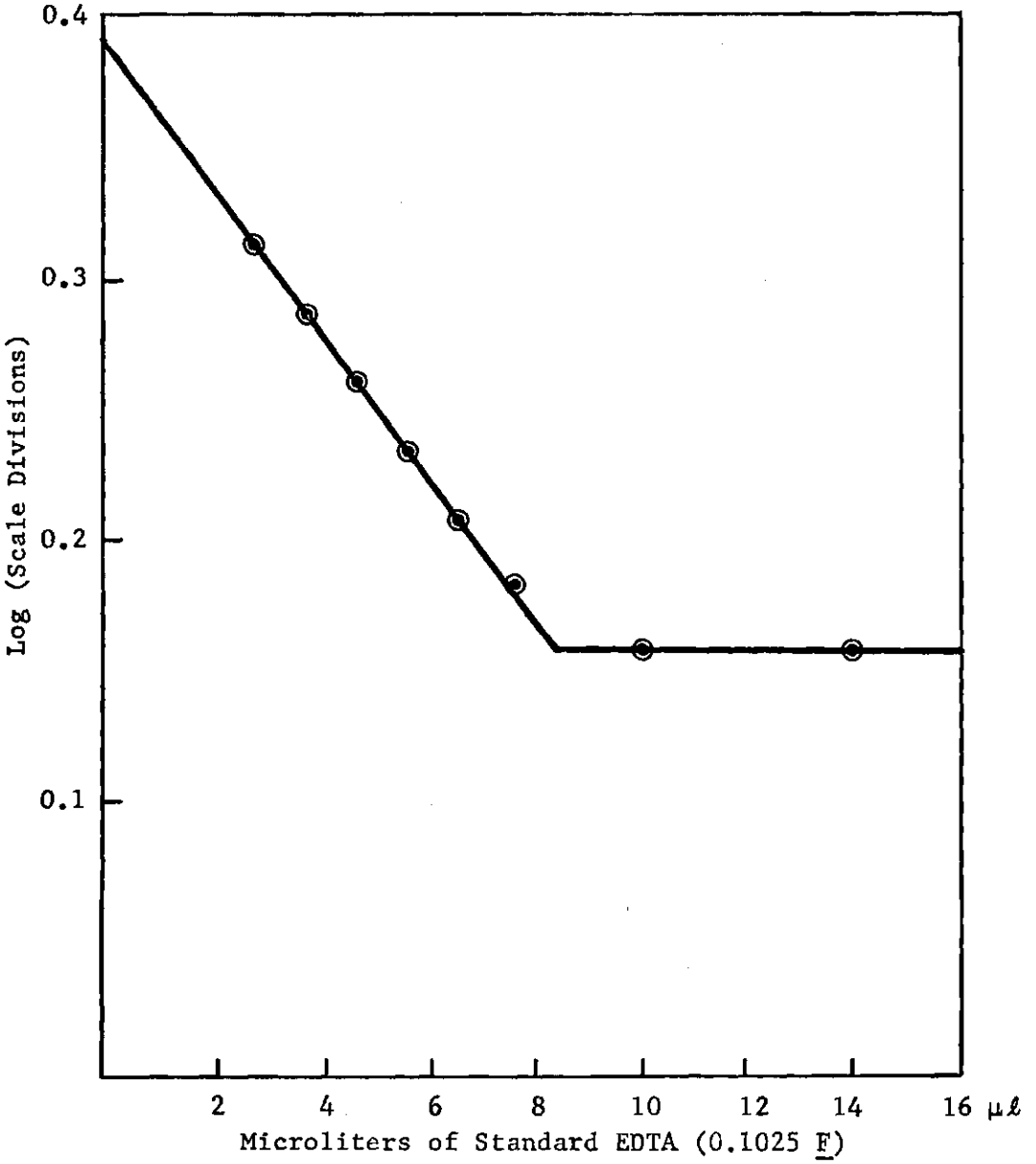

Figure 5. Photometric Titration of Iron in the Presence of Sulfosalicylic Acid

straight line passing through the origin. Such a curve was obtained as is shown in Figure 6. The advantage of this type plot is that no definite value for the formality of either the iron or the EDTA solution is required. The plot can also be used for an assessment of the reproducibility of the method by observing the scatter of the points.

Since the curve is good and the amount of scatter small (as expected because the iron-EDTA system is known to behave well), various amounts of iron solution were carried through the extraction procedure and then titrated. A plot of the data (Figure 7) shows that the extraction behaves well and the precision does not suffer from this additional and quite far-reaching step.

3. Results

So far, rather concentrated solutions of iron and EDTA had been employed, since a volume of 25 ml of iron stock solution corresponds to about 125 μg of iron. Such solutions have been used in order to have comfortable working conditions.

As the next step, a scaling down was performed by appropriately diluting both the iron and EDTA solutions by a factor of 10. Immediately, more EDTA than expected was consumed. It was soon realized that iron impurities in the reagents were responsible for the discrepancies. This was especially true of the hydrochloric acid employed, although high-quality reagent grade had been used. The level of iron tolerated for reagent grade hydrochloric acid is 0.1 μg per ml. While this level is relatively low for most purposes, the situation was intolerable in the present case since large amounts of acid were employed to determine small

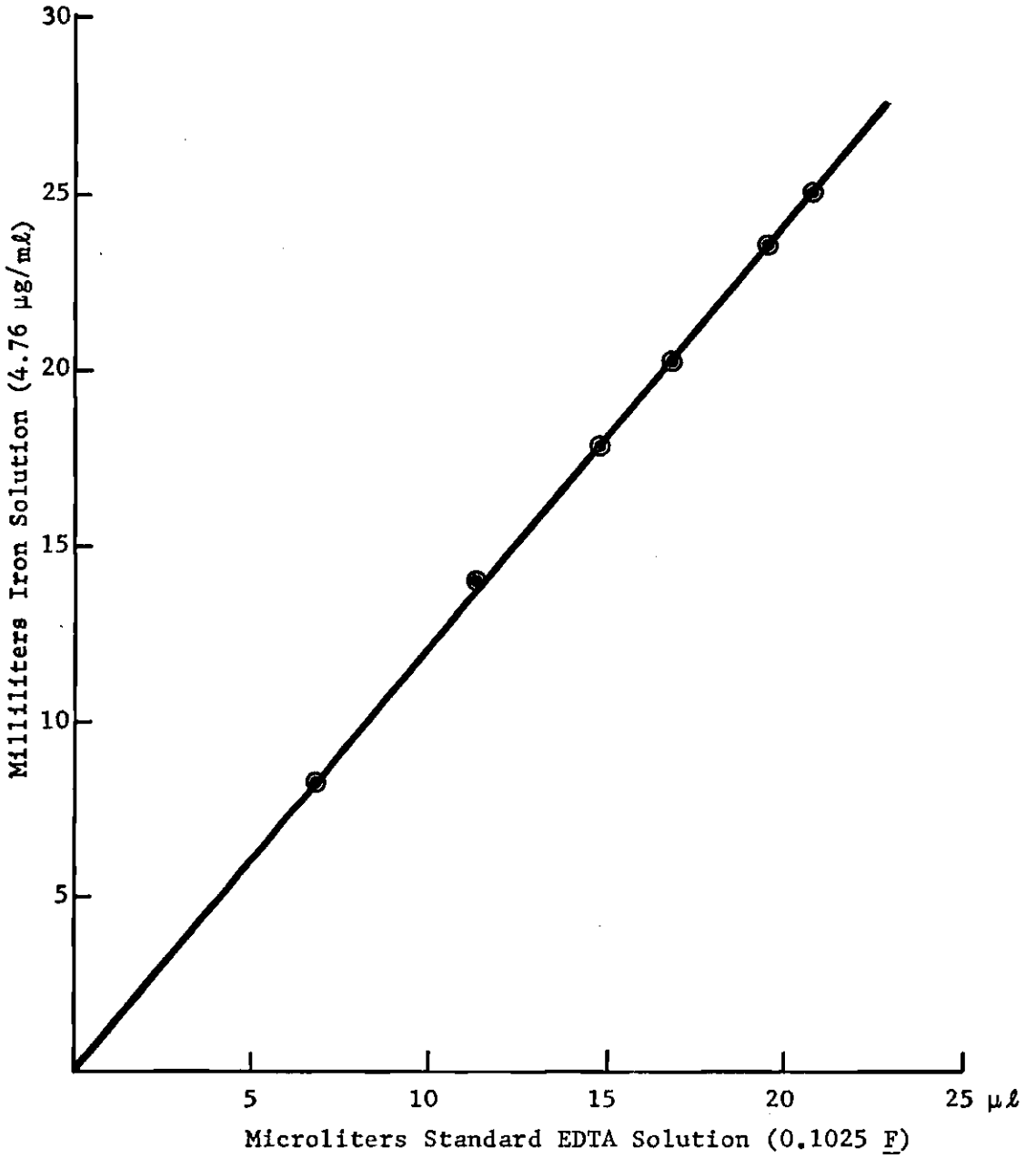

Figure 6. Volume Correlation between Iron and EDTA Solutions (Without Extraction)

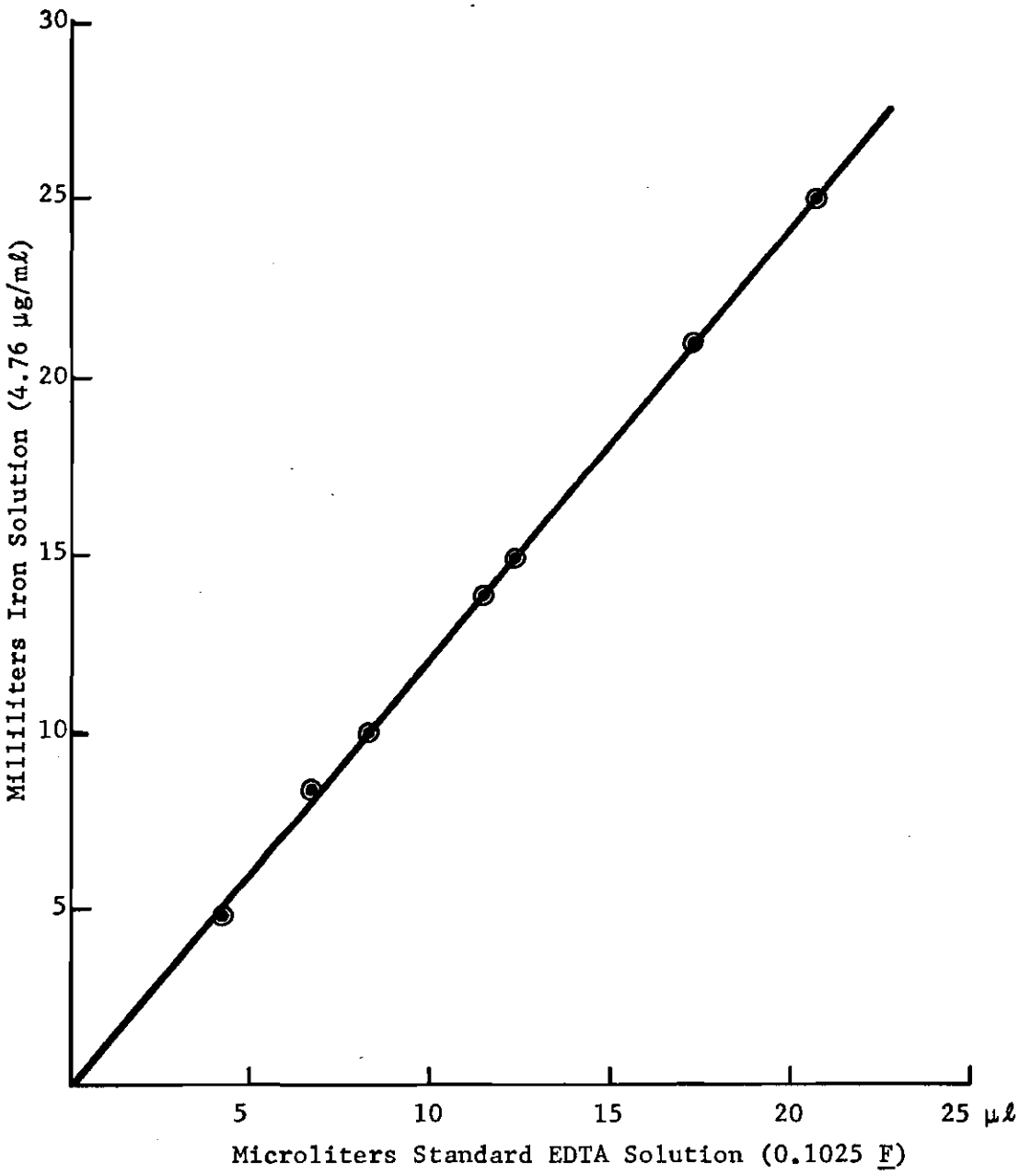

Figure 7. Volume Correlation between Iron and EDTA Solutions (With Extraction)

amounts of iron. Consequently, "iron-free" hydrochloric acid was prepared by bubbling hydrogen chloride gas into high-purity water (that is, distilled water passed through a mixed-bed deionizer).

With this step introduced, the other reagents scrutinized, and their amounts kept to a minimum, the test line shown in Figure 8 was obtained indicating that extraction as well as titration operate quite well even at this low level.

With extreme caution and care employed, it is possible to scale down for another factor of five. However, under the laboratory conditions prevailing in the Lyman Hall Laboratory, the possibility of some iron-containing dust or other interfering material entering the solution was too high to allow frequent reproduction of results. If adequate conditions can be established (in the extreme case, such as working in a dry box), the extraction and titration equilibria are so favorable that they would allow determination of a fraction of a microgram of iron.

The equilibria involved in extraction and titration do not set the limitation, but rather the absorbtivity does. With extracting into the smallest possible aqueous volume and then utilizing the longest possible path length, quite small iron contents could be determined.

Since the main goal of developing an adequate reextraction and a sensitive titration procedure had been achieved, some investigations were conducted to study interferences.

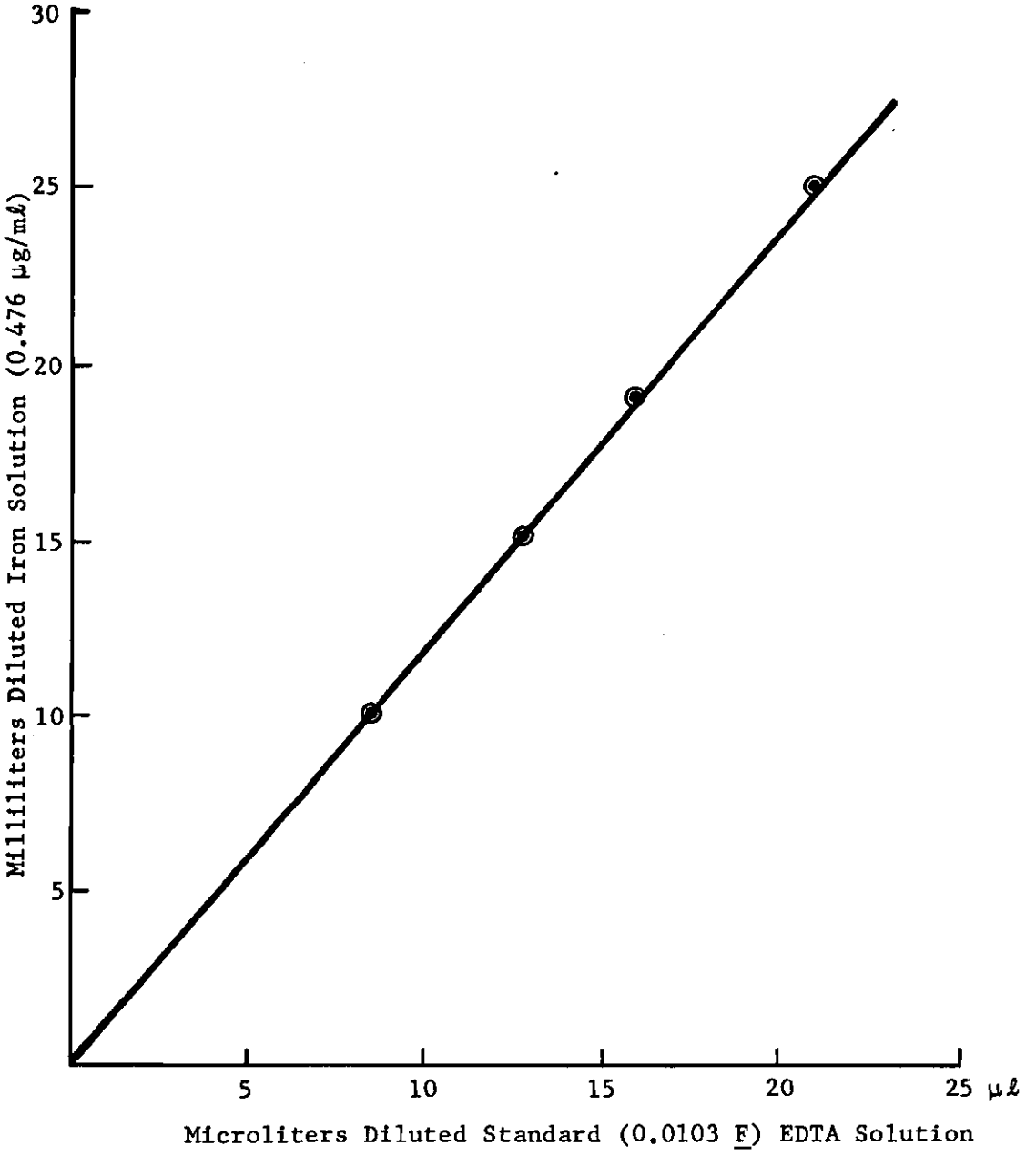

Figure 8. Volume Correlation between Iron and EDTA Solutions; Both Diluted (With Extraction)

CHAPTER V

INTERFERENCE STUDIES

As noted in Chapter III, indium, gallium, copper, and zinc are the only metals that might be expected to interfere during the titration of iron in the proposed method. From knowledge of the present status of EDTA titrations and the conditional stability constants of the indium and gallium EDTA complexes, it is apparent that there is hardly any way to mask these elements during the titration of iron. Therefore, a further separation step would be required. Although the combinations iron-indium and iron-gallium do occur, they are rare and therefore are not included in this study.

Such is not the case with copper and zinc. It is common to find trace amounts of iron in high-purity copper or zinc or their alloys. Also, trace amounts of iron and comparable amounts of copper or zinc may be found in a variety of materials. It is to this latter group that attention was directed in studying the effect of copper or zinc during the photometric titration of iron.

The procedure employed in the interference studies was as described in Chapter IV with the following modification. In step one, the metal ion used as interference was added to the aqueous iron solution before the addition of any other reagents.

Portions of the stock solutions of both copper and zinc were

extracted and the extract was added to the EDTA solution. In both cases, the absorbance change was negligible, indicating the absence of iron.

1. Copper

Copper interferes with the photometric titration of iron when no extraction is performed. This is not an unexpected result as can be seen from inspection of Figure 3 and Table 2 and noting that the ratios of the conditional stability constants, K'_{FeY}/K'_{MY}, for the higher and lower pH ranges are about 10^3 and 10^5, respectively. However, when an extraction is performed, the copper concentration is decreased twenty-five fold, so that it might then be possible to mask the smaller amounts of copper thus making the pertinent (now including the masking agent) conditional stability constant ratio greater than 10^6. As a masking agent for this purpose, thiourea was employed.

However, upon titration of iron in the presence of thiourea, it was found that the results were not reproducible. Although the results were erratic, there was some consistency in that they were always low. It was thought that possibly the thiourea was reducing the iron (III) complex thereby weakening the color of the solution (and at the same time leading to low results) since the iron (II) complex of sulfosalicylic acid does not give a color. This would explain the low results since the reduction of iron (III) by thiourea, although slow, is fast enough to have partially proceeded during the course of the titration. Also, since the titration time was variable, this would explain the fact that the results were erratic. It was found that, upon addition of thiourea to an aqueous iron solution prepared for titration as usual but with no addition

of EDTA, the color of the iron-sulfosalicylic acid complex disappeared.

There are, however, some very good methods for removing the copper. Trace amounts could be removed by utilizing diethyldithiocarbamate and larger amounts could be removed through electrolysis on a mercury pool. Since such is the case, no further time was devoted to the study of copper interference.

2. Zinc

From inspection of Figure 3 and Table 2, it was decided that iron might be titratable in the presence of zinc at the low pH range since the ratio of conditional stability constants in this range is 10^8. Good results can be obtained by this method as seen from Figure 9.

Although the results are good, there is one drawback. In order to obtain reproducible results, a large amount of time must be spent performing a single titration. However, iron can be titrated successfully in the presence of slightly greater than a 16:1 ratio of zinc to iron.

It must be remembered that this corresponds to greater than 100-fold excess of zinc in the original sample. Since this is far above any expected zinc impurity, the situation is much more favorable than first appears.

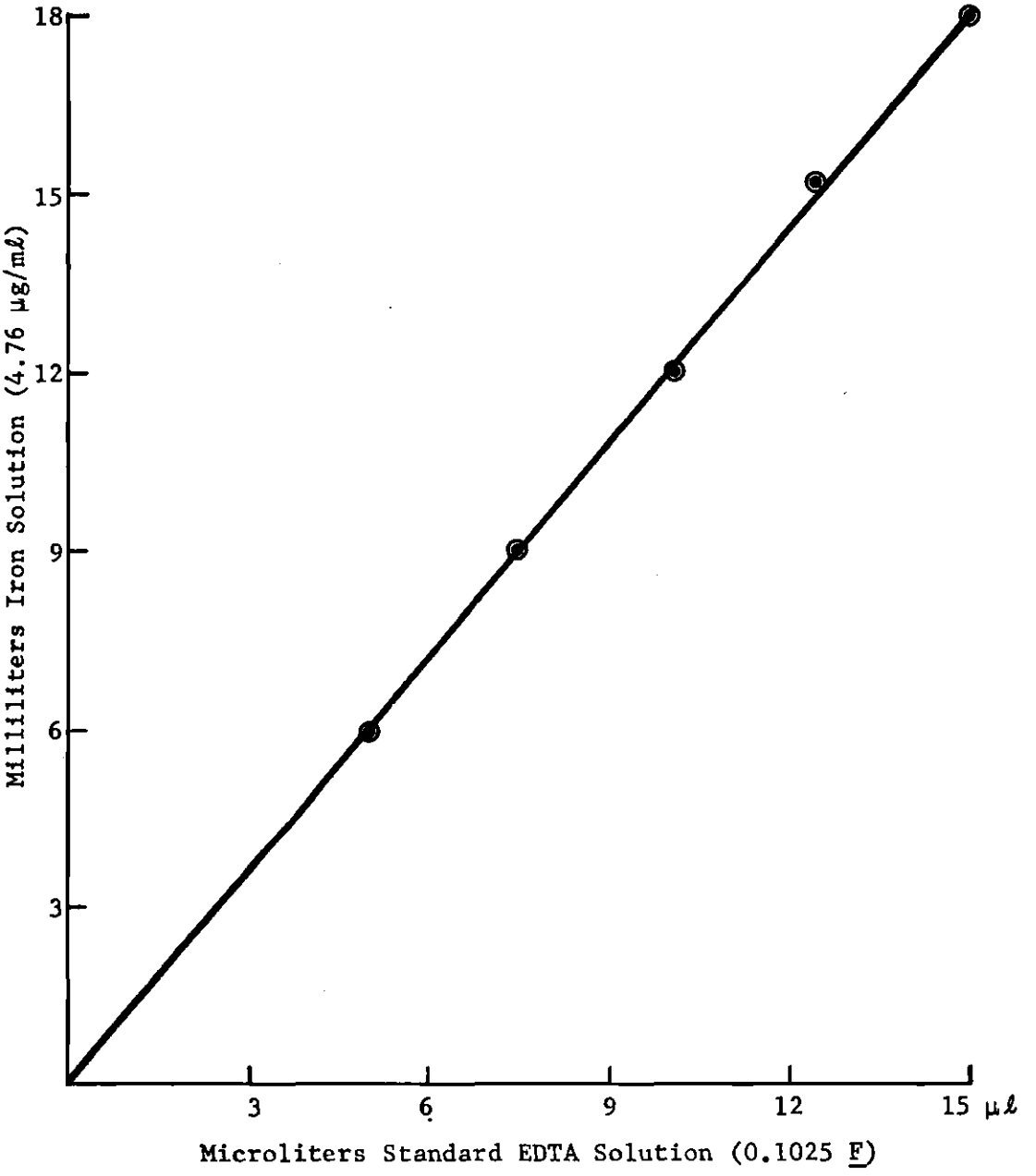

Figure 9. Volume Correlation between Iron Solution, Containing Zinc, and EDTA Solution (With Extraction)

CHAPTER VI

EQUIPMENT AND CHEMICALS

1. Laboratory Equipment

Spectrophotometer

The absorbance curves were obtained with a Spectronic 505 spectrophotometer.

Phototitrator

The photometric titrator used was previously designed and built in this laboratory by R. M. Speights and later modified by J. B. Garrett (11). Titration vessels were constructed using biological microscope slides and delivery was made from a Coleman Microtrator.

pH Meter

All pH measurements were made with a Beckman Zeromatic II pH meter. This device was calibrated with a Beckman pH 4.01 buffer.

Glassware

All volumetric Class A glassware was used with no calibration.

2. Chemicals

Water

Distilled water put through a mixed-bed deionizer was used exclusively.

Acids

duPont concentrated nitric, hydrochloric, and acetic acids were

used.

Bases

J. T. Baker "Analysed" sodium hydroxide pellets were used.

Gases

Matheson Company hydrogen chloride gas was used to prepare an "iron free" solution by bubbling the gas into water which had been distilled and then put through a mixed-bed deionizer.

Disodium(Ethylenedinitrilo)tetraacetic Acid

J. T. Baker "Analysed" disodium EDTA was used. A stock solution was prepared by slurring about 37 g of disodium EDTA in about one-half liter of water. A few pellets of sodium hydroxide were added to hasten dissolution and the solution was diluted to one liter. The resulting solution was about 0.10 F. A one hundred milliliter volume of this solution was diluted to one liter to make a 0.01 F solution which was standardized against a standard zinc solution.

Zinc Standard Solution

A standard 0.1000 F zinc solution was prepared by dissolving 6.538 grams of Baker "Analysed" zinc metal in the minimum amount of nitric acid. The solution was then boiled briefly to expel oxides of nitrogen, cooled, and diluted to one liter.

Iron

A 0.02 F iron solution was prepared by dissolving 2.79 g of iron wire in a minimum amount of nitric acid and diluting to 250 ml. This solution was then standardized against a standard potassium dichromate solution. Appropriate dilutions of the iron solution were made as required.

Copper

A 0.1 F copper solution was prepared by dissolving 6.357 g of copper metal in a minimum amount of 1:1 nitric acid and diluting to one liter.

Salicylic Acid

A 0.1 F salicylic acid solution was prepared by dissolving 6.9 g of salicylic acid in about 300 ml of 95 percent ethanol and diluting to 500 ml.

Sulfosalicylic Acid

A 0.1 F sulfosalicylic acid solution was prepared by dissolving 12.7 g of sulfosalicylic acid in about 300 ml of water and diluting to 500 ml.

Sodium Acetate Buffer

J. T. Baker "Analysed" sodium hydroxide pellets and duPont acetic acid were used to prepare the buffer. Sodium hydroxide (40 g) and concentrated acetic acid (92 ml) were dissolved and diluted to one liter.

Sodium Monochloroacetic Acid Buffer

J. T. Baker "Analysed" sodium hydroxide pellets and J. T. Baker reagent grade monochloroacetic acid were used to prepare the buffer. Sodium hydroxide (20 g) and a solution of monochloroacetic acid (95 g) were dissolved and diluted to 500 ml.

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*Abbreviations used herein follow the form shown in "Index of Periodicals," Chemical Abstracts, 1956.